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[54] COATED PERFUME PARTICLES

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[56] References Cited

U.S. PATENT DOCUMENTS

4,145,184	3/1979	Brain et al.	8/137
4,152,272	5/1979	Young	252/8.8
4,234,627	11/1980	Schilling	427/242
4,636,330	1/1987	Melville	252/174.11

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[57] ABSTRACT

Perfume particles comprise perfume dispersed within certain water-insoluble nonpolymeric carrier materials and encapsulated in a protective shell by coating with a friable coating material. The coated particles allow for preservation and protection of perfumes which are susceptible to degradation or loss in storage and in cleaning compositions. In use, the surface coating fractures and the underlying carrier/perfume particles efficiently deliver a large variety of perfume types to fabrics or other surfaces.

9 Claims, No Drawings

COATED PERFUME PARTICLES

TECHNICAL FIELD

The present invention relates to perfume particles which comprise perfume dispersed within a relatively low molecular weight nonpolymeric carrier material, and encapsulated with a friable coating. Such coated particles are useful, for example, in cleaning and fabric conditioning compositions.

BACKGROUND OF THE INVENTION

This invention is based on the concept of controlled perfume release, i.e., perfume release at a time and under conditions that will achieve the desired perfume effect. In general, this is a very old idea, and various methods for achieving this end have been developed, from the simple idea of putting perfume in wax candles to the complex technology of microencapsulation.

One aspect of the concept of controlled release of perfume is providing slow release of perfume over an extended period of time. This is generally achieved by blending perfume with a substance that will, in essence, "trap" the perfume so that small amounts of perfume are released over time. The use of high molecular weight polymeric substances having perfume incorporated therein to provide controlled release of perfume over time is known. See, for example, U.S. Pat. No. 4,184,099 Lindauer et al, issued Jan. 15, 1980; European Patent Application 0 028 118, Leonard, published May 6, 1981; and U.S. Pat. No. 4,110,261, Newland, issued Aug. 29, 1978, which teach combining perfume with a release controlling medium and forming the combination into a solid product for air freshening.

Textile laundering is also concerned with controlled release of perfumes. Application of this concept allows for slowing down or preventing release of perfume through long periods of shelf storage. Such a concept also allows for using much lower levels of perfume in product since much less perfume is wasted.

Perfume preservation over storage times can be achieved in a variety of ways. The perfume can be made a part of the package for the composition. The perfume can be combined with plastic used to make a bottle, or the perfume can be mixed with a polymer substance and the product used to coat a cardboard package composition, as is disclosed in U.S. Pat. No. 4,540,721, Staller, issued Sept. 10, 1985. Either way the perfume is released over time from the polymer matrix.

The perfume/controlled release agent may also be in the form of particles mixed into the laundry composition. One method taught to achieve this end is combining the perfume with a water-soluble polymer, forming into particles and adding to a laundry composition, as is described in U.S. Pat. No. 4,209,417, Whyte, issued June 24, 1980; U.S. Pat. No. 4,339,356, Whyte, issued July 13, 1982; and U.S. Pat. No. 3,576,760, Gould et al, issued April 27, 1971.

The perfume may also be adsorbed onto a porous carrier material, which may be a polymeric material. See, for example, U.K. Patent Publication 2,066,839, Bares et al (applied for in the name of Vysoka Skola Chemicko Technologika), published July 15, 1981. These methods may also be used to mask unpleasant odors in a composition or to protect perfume from degradation by harsh components in a laundry composition. Such methods will provide these benefits only for dry powder or granular type compositions because, as soon as the polymer is hydrated the perfume is released. Thus, these methods provide for perfume fragrance benefits upon opening of the product package and loading into the washing apparatus. While these benefits are desirable, it would be even more desirable to have a method which allows for delivery of undiluted, undissipated and unaltered perfume to fabric and release of the perfume at the end of the laundry process so that the fabric is scented with the desirable perfume odor.

Of course, one method for achieving this end is putting the perfume into a product which goes directly into the dryer. This way, the perfume is delivered to the fabric in the dryer cycle. Such a method is taught in both U.S. Pat. No. 4,511,495, Melville, issued Apr. 16, 1985, and U.S. Pat. No. 4,636,330, Melville, issued Jan. 13, 1987. Both teach forming perfume into particles with a carrier. These particles are then formulated into a composition which is applied to textiles prior to putting into the dryer or prior to clothes-line drying.

An even more desirable method for delivering perfume to laundered fabric would be one which provides for protection of the perfume through the washing process and hence delivery of the perfume to fabric in essentially its original state.

Such a method must allow for prevention of dilution, degradation or loss of the perfume during the wash cycle of the laundry process. This is done by utilizing a system that releases the perfume in the drying process or later after the perfume has been delivered to the fabric. Preventing release of perfume during the washing process involves very different and more difficult technology. Such protection must be stable in not only the heat-elevated conditions of the wash but must also be stable against degradation by water and other harsh chemicals in the washing process such as bleach, enzymes, surfactants, etc.

One method which has been developed to provide these benefits is perfume microencapsulation. Here the perfume comprises a capsule core which is coated completely with a material which may be polymeric. U.S. Pat. No. 4,145,184, Brain et al, issued Mar. 20, 1979, and U.S. Pat. No. 4,234,627, Schilling, issued Nov. 18, 1980, teach using a tough coating material which essentially prohibits the diffusion out of the perfume. The perfume is delivered to fabric via the microcapsules and is then released by rupture of the microcapsules such as would occur with manipulation of the fabric.

Another method of perfume delivery involves providing protection of perfume through the wash cycle, with release of perfume in the heat-elevated conditions of the dryer. U.S. Pat. No. 4,096,072, Brock et al, issued June 20, 1978, teaches a method for delivering fabric conditioning agents to textiles through the wash and dry cycle via particles containing hydrogenated castor oil and a fatty quarternary ammonium salt. Perfume may be incorporated into these particles. However, it is not clear whether the perfume thus incorporated is released in the wash cycle or carried in the particles to the dryer and released there, as the particles soften.

U.S. Pat. No. 4,402,856, Schnoring et al, issued Sept. 6, 1983, teaches a microencapsulation technique which involves the formulation of a shell material which will allow for diffusion of perfume out of the capsule only at certain temperatures. This allows for maintenance of the perfume particles through storage and additionally through the wash cycle. The particles adhere to the fabric and are carried over to the dryer. Diffusion of the perfume out of the capsules then occurs only in heat-elevated conditions of the dryer. These particles are made of gelatin, an anionic polymer and a hardening agent.

U.S. Pat. No. 4,152,272, Young, issued May 1, 1979, teaches incorporating perfume into waxy particles to protect the perfume through storage in dry compositions and through the laundry process. The perfume then diffuses through the wax matrix of the particles on the fabric in the heat-elevated conditions of the dryer.

It is desirable to provide compositions comprising perfume particles that can be incorporated in liquid as well as dry granular or powder compositions and provide long-term storage stability.

It is desirable to provide a method for delivering a broad range of perfume materials to fabric or other surfaces during a cleaning or fabric- or fiber-conditioning process.

It would be most desirable to have a perfumed cleaning or conditioning composition which would provide improved product odor, improved odor of perfume released during the cleaning process, and improved odor and intensity of perfume delivered to the surface being cleaned.

It would be particularly desirable to provide perfumed particles which are stable in fluid compositions, but which liberate their perfume, in use.

SUMMARY OF THE INVENTION

Apart from being especially effective in providing their intended benefit of prolonged perfume release, the coated perfumed particles of the present invention are designed to provide several important advantages over the various encapsulated perfumes of the art. First, the preferred coatings used herein are stable not only in solid or granular laundering compositions, but also in liquid compositions. Second, the coated perfumed particles herein do not require any additional treatment, such as the application of additional cationic coatings, to achieve the desired result of substantivity to fibers and fabrics. Third, using solid carrier materials as the "cores" of the particles herein makes the particles less fragile than perfume particles having liquid cores. This not only simplifies manufacture, but also means that the particles are more robust under storage and shipping conditions in laundering and other types of compositions. The nonpolymeric carrier materials used herein have the additional advantage over many polymeric perfume carriers in that they are degradable in the environment or in sewage treatment facilities and/or that they are available from renewable resources such as plant and animal fats and oils. Moreover, the particles herein allow for the formulation of condensed detergent granules with desirable perfume levels, but without the undesirably high odor levels in the product package that would be associated with the use of raw perfume.

However, in order to achieve the above-described benefits and yet function in the intended manner as a perfume delivery vehicle, it is important that the perfume-carrying materials employed herein be carefully selected from among the various classes of prospective perfume carrier materials broadly disclosed in the art. For example, the carrier should be somewhat polar so that it will imbibe a considerable amount of a wide variety of perfume ingredients. Fatty alcohols and esters meet this requirement, but fatty acids tend to be too polar to imbibe the desired high levels of many perfume ingredients. The carrier should be solid at room temperature so that stable particles can be produced and stored, yet must be somewhat softenable, in-use, to help release the perfume. Again, fatty alcohols and esters meet these requirements. Moreover, the carriers should be substantially water-insoluble (as defined more fully hereinafter) under usage conditions, since they would otherwise completely dissipate their perfume into the aqueous medium, e.g., laundry liquors, in which they are used. Fatty alcohols and esters also meet these requirements. It is also important that the core material be selected to be "compatible" with the material used to make the friable coating. This is especially important to provide coated particles with good integrity of the preferred friable aminoplast polymer coatings discloser hereinafter. While not intending to be bound by theory, it appears that the polarity of the alcohols and esters makes them especially useful with such coatings.

Moreover, it has now been determined that the most highly preferred perfume particles of the present invention have optimal size requirements which are somewhat more stringent than various encapsulated perfumes known in the literature in order to perform optimally in laundering products of the type disclosed herein.

The present invention encompasses perfume particles having an average size, when coated, of less than about 350 microns (preferably, an average size not greater than 150 microns; most preferably a size range of 100-150 microns) which comprise from about 5% to about 50% (preferably, at least about 10%) of a perfume dispersed in from about 50% to about 95% of a nonpolymeric fatty alcohol or fatty ester, or mixtures thereof, carrier material having a molecular weight of from about 100 to about 500 and a melting point of from about 37° C. to about 80° C., said esters or alcohols being substantially water-insoluble, said particles having a substantially water-insoluble friable coating on their outer surfaces. (By "size" herein is meant average particle diameter for substantially spherical particles, or the size of the largest diameter or dimension for nonspherical particles.) Particle sizes larger than this may be lost from the surface they are deposited on, and do not provide a relatively large enough surface area to release the perfume at the desired rate. Also, particles larger than specified herein may be undesirably noticeable on the surface being treated. Particles at the low end of the range tend to adhere well to the surface being treated, but tend to release the perfume quite rapidly. Extremely small particles outside the low end of the range tend to be rinsed off fabrics during laundering.

Typically, the particles herein are characterized by a coating which comprises up to about 30% by weight of the perfumed particles. For general use in fabric laundering and conditioning compositions, the coating typically comprises from 1% to 20%, preferably 10% to 20%, by weight of the perfumed particles.

Preferred particles herein are those wherein the friable coating is substantially water-insoluble. Suitable coatings of this type can be prepared from aminoplast polymers, e.g., the reaction products of an amine and an aldehyde. Typical friable coatings comprise, for example, the reaction products of an amine selected from urea and melamine, and an aldehyde selected from formaldehyde, acetaldehyde and glutaraldehyde, and mixtures of said amines and said aldehydes. Such friable coatings are described hereinafter.

The coated perfume particles herein are useful in situations where the particle coating is ruptured or worn away (e.g., in an automatic washing machine or laundry dryer) to release the particles, which, in turn, release their perfume. Thus, the coated particles are useful in typical cleaning composition, comprising detersive surfactants, optional builders, and the like. The particles are likewise useful in conditioning compositions, comprising fiber- and fabric-conditioning agents.

As can be seen from the foregoing and from the disclosures hereinafter, the present invention encompasses not only novel and useful perfumed particles and compositions containing same, but also encompasses a method for delivering perfume-releasing particles to the surface of fabrics undergoing a laundering or softening process in a laundering apparatus, comprising adding to said laundering apparatus a detergent composition or a fabric softening composition containing particles comprising the core/perfume/ friable coating, as disclosed in detail herein, and operating said apparatus in standard fashion with agitation of the machine liquor and fabrics, whereupon the agitation associated with said operation ruptures the coating on said particles, or fractures the particles themselves, sufficiently to allow release of the perfume when said particles become deposited onto said fabrics during said laundering or softening process.

In a highly preferred mode, the process herein employs particles comprising: 55–65% by weight of the core material as a C_{14}-C_{18} alcohol, especially straight-chain alcohols, or mixtures thereof; from 20–30% by weight of the perfume; and the balance comprising a friable coating, especially water-insoluble polymeric coatings made from an amine such as urea, melamine, or mixtures thereof, plus an aldehyde selected from formaldehyde, glutaraldehyde, or mixtures thereof.

It will be appreciated that the method herein is similarly useful in fabric bleaching operations which are carried out under conditions of sufficient agitation to fracture the friable coatings, or which rupture the particles themselves. Likewise, the method herein is suitable for releasing perfume particles from bar soap and/or shampoos, and the like, provided that such compositions are used, e.g., rubbed, with sufficient vigor to fracture the coating on said particles, or the particles themselves.

All percentages herein are by weight, unless otherwise specified.

DETAILED DESCRIPTION OF THE INVENTION

The present invention allows for preservation, protection, and delivery of perfumes contained in cleaning and conditioning compositions through extended storage and harsh cleaning conditions. This is achieved by isolation of the perfume in a carrier material in the form of small particles. The individual components of the invention will now be discussed in detail.

The Perfumed Particles

The perfumed particles of the present invention comprise perfume dispersed in certain carrier materials. The perfumed particles are coated with a friable coating material which ruptures in-use to release the perfumed particle which, in turn, releases its perfume.

In the present context, the term "perfume" means any odoriferous material or any material which acts as a malodor counteractant. In general, such materials are characterized by a vapor pressure less than atmospheric pressure at ambient temperatures. The perfume or deodorant materials employed herein will most often be liquid at ambient temperatures, but also can be solids such as the various camphoraceous perfumes known in the art. A wide variety of chemicals are known for perfumery uses, including materials such as aldehydes, ketones, esters and the like. More commonly, naturally occurring plant and animal oils and exudates comprising complex mixtures of various chemical components are known for use as perfumes, and such materials can be used herein. The perfumes herein can be relatively simple in their composition or can comprise highly sophisticated, complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odor.

Typical perfumes herein can comprise, for example, woody/ earthy bases containing exotic materials such as sandalwood oil, civet, patchouli oil and the like. The perfumes herein can be of a light, floral fragrance, e.g., rose extract, violet extract and the like. The perfumes herein can be formulated to provide desirable fruity odors, e.g., lime, lemon, orange and the like. Suitable perfumes include musk ambrette, musk ketone, musk tibetine, musk xylol, aurantiol, ethyl vanillin and mixtures thereof.

Perfume materials such as these are described more fully in S. Arctander, *Perfume Flavors and Chemicals, Vols. I and II,* Aurthor, Montclair, N.J., and the *Merck Index. 8th Edition,* Merck & Co., Inc. Rahway, N.J., both references being incorporated herein by reference.

In short, any chemically compatible material which exudes a pleasant or otherwise desirable odor can be used in the perfumed particles herein to provide a desirable odor when applied to fabrics.

Perfumes which are normally solid can also be employed in the present invention. These may be admixed with a liquefying agent such as a solvent prior to incorporation into the particles, or may be simply melted and incorporated, as long as the perfume does not sublime or decompose upon heating.

The invention also encompasses the use of materials which act as malodor counteractants. These materials, although termed "perfumes" hereinafter, may not themselves have a discernible odor but can conceal or reduce any unpleasant odors. Examples of suitable malodor counteractants are disclosed in U.S. Pat. No. 3,102,101, issued Aug. 27, 1963, to Hawley et al.

The perfumed particles of the present invention can even comprise perfumes which are not typically used to deliver a fragrance to a surface, such as fabric through the laundry process. Perfume materials which are very volatile, unstable, or soluble in the particular compositions being used to deliver the perfume may be used in the present invention because the perfume is isolated from the composition in the particles. Perfume materials which are not substantive to fabrics in the laundry process can also be used in the present invention since the particles deliver the perfume to the fabric surface where it is released. Thus, use of the present invention to deliver a perfume to a surface broadens the class of perfume materials that can be utilized.

Generally, the perfumed particles of the present invention will comprise from about 5% to about 50%, preferably from about 20% to about 30%, perfume. The exact amount of perfume used in the particles will vary greatly depending on the strength of the particular fragrance used, and the desired odor effect.

The carrier materials employed herein are characterized by several criteria which make them especially suitable in the practice of this invention. Of course, toxicologically-acceptable and non-skin irritating materials are used. As noted above, degradable materials and/or materials which are available from renewable resources are used. In general, the materials are solids at room temperature have a melting point within the range noted hereinabove. This will prevent melting of the particles in storage. (It is most desirable to have a carrier material that will not completely melt in an automatic dryer, to avoid blocking of the lint screen and excessive build-up of heat in the dryer). The melting point of the carrier material should also not be higher than a point at which the perfume to be combined therewith will decompose. The melting point of the carrier material is measured by what is called the drop melting point method. American Society for Testing and Materials (ASTM) Test Method D127-63 (reapproved 1982, incorporated by reference herein). Briefly, this method involves the following. The sample to be measured is deposited onto a thermometer bulb by dipping a chilled thermometer into the melted sample. The thermometer bearing the sample is then placed into a test tube and heated by means of a water bath until the sample melts and the first drop falls from the thermometer bulb. The average of the temperatures at which the drops of sample fall is the drop melting point of the sample.

The carrier material should also be inert to the perfume and relatively odorless. The material must allow for diffusion of the perfume therethrough. The carrier material must also be such that it melts without decomposition.

Having thus described the carrier materials useful herein with regard to their physico-chemical properties, the following illustrates various nonpolymeric compounds which can be used as carrier materials herein.

One class of carrier materials which is highly preferred herein comprises the fatty alcohols. The fatty alcohols of chain of at least C_{14} are substantially water-insoluble. Substantial water-insolubility is an important feature of the carrier materials in-use, since if the particle dissolves, e.g., in a laundering liquid, it releases its perfume immediately and thus does not deposit onto fabrics to provide the intended prolonged release of said perfume. Accordingly, by "substantially water-insoluble" herein is meant that the carrier materials will not be dissolved in water to an extent greater than about 10%, preferably not greater than 5%, by weight, at the temperatures of the aqueous media in which they are used.

Moreover, fatty alcohols are typically solid at room temperature, i.e., they have a melting point above about 30° C., and typically will melt over the range of about 37° C. to about 75° C. The most highly preferred carrier materials of this class will be selected from molecules which will not undesirably interact with the perfumes which they are carrying, nor have a substantial amount of undesirable odor characteristics of their own. For example, the preferred alcohol carriers described hereinafter will, in general, preferably not be contaminated with lower molecular weight alcohols or fatty acids which could result in "goaty" or rancid odors, unless, of course, such odors are a desired complement to the perfume being carried. In particular, the straight-chain fatty alcohols are preferred, since they are available from natural sources. However, branched-chain and some unsaturated alcohols may also be used.

Among the fatty alcohol class of carriers, those in the C_{14}–C_{18} chain length are most preferred. For reasons of possible malodor, as noted above, it is generally preferred that the alcohols be substantially free of C_4–C_{10} chain-length alcohols and their fatty acid oxidation products. More specifically, n-$C_{14}OH$ (myristyl alcohol/tetradecanol) is preferred under lower temperature laundering conditions in the United States, whereas C_{16}–C_{18} alcohols can be used under the somewhat higher temperature laundering conditions found in some European countries. Higher alcohols are also desirable where a long-lasting perfume benefit is desired. C_{12} alcohols can also be present in the cores. However, it will be appreciated that cores containing substantial amounts of C_{12} alcohols may liquify under some warehouse storage conditions, and the resulting liquid core/coated particles are more fragile than solid core/ coated particles, and are subject to fracture when the product is shipped. The C_{20}–C_{24} alcohols are also useful under some conditions, although these latter materials are in considerably shorter supply than the C_{14}–C_{18} materials and are, consequently, more expensive. Mixtures of the fatty alcohols may also be used, provided that they meet the above-noted criteria.

In addition to the alcohols noted hereinabove, the following are representative, nonlimiting examples of alcohols which can be used as the core materials herein: n-pentadecanol, n-hexadecanol, n-heptadecanol, n-octadecanol, n-docosanol, n-heneicosanol, 16-methylheptadecanol, 26-methylheneicosanol, 22-methylpentacosanol, and D-18-methyleicosanol.

Other nonlimiting examples of nonpolymeric carrier materials useful herein include various esters having melting points of at least about 30° C., preferably from about 37° C. to about 75° C. The same considerations regarding substantial water-insolubility, acceptable odor characteristics, etc., noted for the alcohols are also important factors to be considered with the ester perfume carrier materials.

In general, the esters will comprise at least about 18 carbon atoms. Suitable esters include, for example, lower (typically C_1–C_4) alkyl esters of fatty acids which, chemically, comprise fatty acid esters of lower monohydric alcohols. Likewise, various fatty acid esters of polyhydric alcohols can be employed herein, as long as the water-insolubility parameter is met. Fatty acid triglycerides, e.g., "fats", meeting the foregoing parameters are also suitable for use herein, assuming proper deodorization.

The following examples of suitable ester carrier materials are given by way of illustration, and not by way of limitation. It will be appreciated by those skilled in the art that such esters are commercially available from various sources. Such esters include: methyl stearate; ethyl stearate; methyl nonadecylate; ethyl nonadecylate; methyl arachidate; methyl behenate; the monostearyl and monopalmityl esters of ethylene glycol; the monostearyl and monopalmityl esters of propylene glycol; the monostearyl and monopalmityl esters of trimethylene glycol. Various diesters of the foregoing polyols can also be used, based on their melting points and solubility characteristics.

In a typical process, the perfume-containing particles can be made as follows. The carrier material is first heated slowly to its melting point. The material is not heated any more than is necessary to just melt the substance. The perfume is then quickly added, generally as an oil or liquid, at room temperature to the melted carrier substance. The two are quickly mixed into a homogeneous blend then rapidly cooled with liquid nitrogen (or with dry ice or any other means which will cool the mixture quickly) until it has completely solidified. The solid material is then subdivided, generally by grinding or milling, to produce particles of the desired average size. Other methods such as spray cooling or extrusion may also be used to subdivide the particles.

To further stabilize particularly volatile or delicate perfumes, it may be desirable to preload the perfume (i.e., mix the perfume) onto silica gel or clay prior to combining with the carrier substance. Some perfumes which are not so volatile will not require this special treatment because it would inhibit their release from the carrier substance too much. Optimization of the rate at which the perfume is released from the carrier is the goal, and this optional additional step allows for better control of that rate with some of the more volatile perfumes.

The Coating

The perfume-containing particles, above, are encapsulated to provide a friable coating. This coating prevents the perfume from diffusing out of the particles as readily during long storage periods. Moreover, the coating helps preserve the original "character" of perfumes having particularly volatile top-notes. Moreover, the coating helps protect the perfumed particle from other ingredients in the formulation being perfumed.

The coating materials used herein are friable, and are designed to break-up as the perfumed formulation is used, thereby releasing the perfumed particle.

The particles may be coated with more than one friable coating material to produce a particle having more than one layer of coating. Different coating materials can be chosen to provide different perfume protection as needed, so long as one of the coatings, generally, the outermost, is friable.

The individual perfume-containing particles may also be agglomerated with the coating material to provide larger particles which comprise a number of the individual perfume-containing particles. This agglomerating material surrounding the particles provides an additional barrier to diffusion of the perfume out of the particles. Such an approach also minimizes the surface area of free particles susceptible to perfume diffusion. The ratio of perfume particles to agglomerate material will vary greatly depending upon the extent of additional protection desired. This agglomeration approach may be particularly useful with very volatile perfumes or perfumes that are especially susceptible to degradation. Also, agglomeration of very small perfume particles would provide additional protection against premature diffusion out of perfume.

Agglomeration of particles in this fashion is useful in preventing segregation of small perfume particles from larger detergent granules, for example, in a dry granular detergent product.

Process of Manufacture

For friable coatings, the process of manufacture is based on applying the coating as a kind of "shell" to the perfumed particles. For perfumed particles whose carrier material has a melting point below that of the boiling point of the solvent used in the process, the process involves adding the carrier and perfume to a solvent solution of the "shell" material, or a suitable precursor, held above the carrier melting temperature. The system is agitated sufficiently to form an emulsion of the carrier/perfume of desired liquid drop size in the shell solution. The conditions necessary to deposit the encapsulating material are then established and the whole is cooled to give encapsulated solid particles having the desired, friable "shell". Water insolubility of the shell is established either at the deposition stage, or by suitable treatment prior to isolation or use of the particles.

Although the process described here is a one step molten drop formation/encapsulation procedure, it should be readily apparent to those skilled in the art that encapsulation of pre-formed perfume particles can be accomplished in a like manner. The pre-formed particles can be prepared in a variety of ways, including cryogrinding, spray drying, spray congealing and meltable dispersion techniques such as those described in books by P. B. Deasy ("Microencapsulation & Related Drug Processes", Dekker, N.Y., 1986) and A. Kondo ("Microcapsule Processing and Technology", Dekker, N.Y., 1979). Such techniques would be required for carrier materials having a melting point above the solvent boiling point.

A variety of suitable encapsulation procedures can be used, such as reviewed in the books by Deasy and Kondo above. Depending on materials used, the shell can impart hydrophilicity or hydrophobicity to the particles. For examples of encapsulating materials and processes including gelatin-gum arabic concentrate deposited by a complex coacervation procedure, see, e.g., U.S. Pat. No. 2,800,457, and urea-formaldehyde deposited by a polycondensation process, e.g., U.S. Pat. No. 3,516,941. Water insolubility of shell materials may be imparted, for example, by cross-linking of gelatin-gum arabic coacervate with suitable aldehydes or other known gelatin hardeners after deposition. Polymerization of the urea-formaldehyde precondensate during an encapsulation process inherently yields water-insolubility.

The slurry containing the perfume particles can be used directly, e.g., admixed and dried with other components of the granular detergent formulations, or the particles can be washed and separated, and dried if desired.

EXAMPLE I

Perfume particles containing a hydrophobic, water-insoluble, friable coating deposited by polycondensation are prepared as follows.

A urea-formaldehyde precondensate is first formed by heating a mixture of 162 g 37% aqueous formaldehyde and 60–65 g urea, adjusted to pH 8.0 with 0.53 g sodium tetraborate, for 1 hour at 70° C., and then adding 276.85 g water.

429 ml of this precondensate and 142 ml water are then stirred in a 1-l steel reactor and 57.14 g sodium chloride and 0.57 g sodium carboxymethyl cellulose added. Then are added the core components comprising 166.2 g $C_{14}OH$ carrier and 55.8 g perfume, and the reactor is heated to about 90° C. Agitation is adjusted to emulsify and maintain the molten core at the desired drop size, and the pH of the contents is adjusted to about 5.0 with dilute hydrochloric acid.

The reactor is then allowed to cool to room temperature with a gradual pH reduction to 2.2 over a 2 hour period. The reactor is then increased to about 50° C. for a further 2 hours, then cooled to room temperature, after which the pH is adjusted to 7.0 with 15% N ammonium hydroxide solution.

The resultant slurry containing the solid core particles encapsulated with urea-formaldehyde polymer may be used directly, or may be isolated by separation, washing and air drying as required.

The coated perfumed particles prepared in the foregoing manner can be used in all types of products where it is desirable to deposit fragrances on treated surfaces, and wherein sufficient agitation or pressure is exerted to rupture the friable coating. Typical examples of such products are laundry detergents and fabric softeners. The following illustrates the use of the compositions of this invention in such products.

Laundry cleaning products comprise: a detersive surfactant (typically 5%-30% wt.); optionally but typically, one or more detergency builders (10%-55% wt.); optionally, 3%-20% wt. of various enzymes, bleaches, carriers, and the like, all well-known from standard texts and very familiar to detergent formulators. Surfactants include soap, alkyl benzene sulfonates, ethoxylated alcohols, alkyl sulfates, alpha-sulfonated fatty acids, and the like. Builders include various phosphates, zeolites, polycarboxylates and the like. U.S. Pat. Nos. 3,985,669, 4,379,080 and 4,605,609 can be referred to for typical listings of such ingredients.

Modern fabric softeners typically comprise about 3%-35% wt. of one or more quaternary ammonium salts, e.g., ditallowdimethyl ammonium chloride or imidazoline or imidazolinium compounds. Softeners (and antistatic agent) generally have one, or preferably two, C_{12}-C_{18} alkyl substituents and two or three short chain alkyl groups. Again, such materials are conventional and well-known to softener formulators.

It is to be understood that one of the major advantages of the coated perfumed particles of this invention is their ability to be stably formulated (typically 0.1%-10% wt.) in combination with conventional detergent, bleach and fabric treatment compositions without difficulty.

EXAMPLE II

A granular laundry detergent is as follows:

Component	Weight %
Sodium C_{13} alkylbenzene sulfonate	7.5
Sodium C_{14-15} alkylsulfate	7.5
C_{12-13} alkyl polyethoxylate (6.5) stripped of unethoxylated alcohol and lower ethoxylate	2.0
C_{12} alkyltrimethyl ammonium chloride	1.0
Sodium tripolyphosphate	32.0
Sodium carbonate	10.0
Sodium perborate monohydrate	5.3
Sodium octanoyloxybenzene sulfonate	5.8
Sodium diethylene triamine pentaacetate	0.5
Sodium sulfate, H_2O and minors	Balance

The above composition is prepared using conventional means. The composition is combined with the perfume particles of Example I as follows. An amount of the perfume particles of Example I is combined with the detergent composition so that the detergent composition comprises about 0.3% perfume.

The particles may be simply mixed in with the detergent granules. To prevent segregation of the perfume particles during packaging and shipping (due to their smaller size relative to the detergent granules), the particles can optionally be coated or agglomerated with a water-soluble coating material (on top of the friable coating) prior to combining with the detergent granules. This can be accomplished with a Schugi mixer (Flexomix 160) where a sufficient amount of a dextrin glue solution (2% dextrin, 3% water) is sprayed onto the particles to result in agglomerates of perfume particles in the same size range as other detergent granules.

The perfume is protected in the particles from degradation by the bleach in the detergent composition over long periods of storage. When used in the laundry process in an automatic washing machine this detergent composition will provide perfume fragrance in substantially its original state from product, through the wash process and onto the fabric.

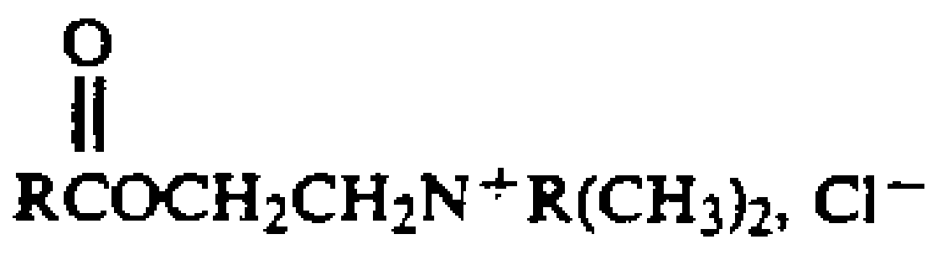
A great number of perfumes can be utilized in the present composition that would not otherwise be appropriate for use in such laundry detergent compositions.

EXAMPLE II

A liquid fabric softener for use in an aqueous laundry rinse bath is as follows:

Component	Weight %
Softener A*	3.00
Softener B**	5.00
HCl	0.29
Polydimethylsiloxane	0.15
Polyethylene Glycol (4000)	0.30
Bronopol (Antimicrobial)	100 ppm
Calcium Chloride	30 ppm
Dye	30 ppm
Coated Perfume Particles***	4.0
Water	Balance

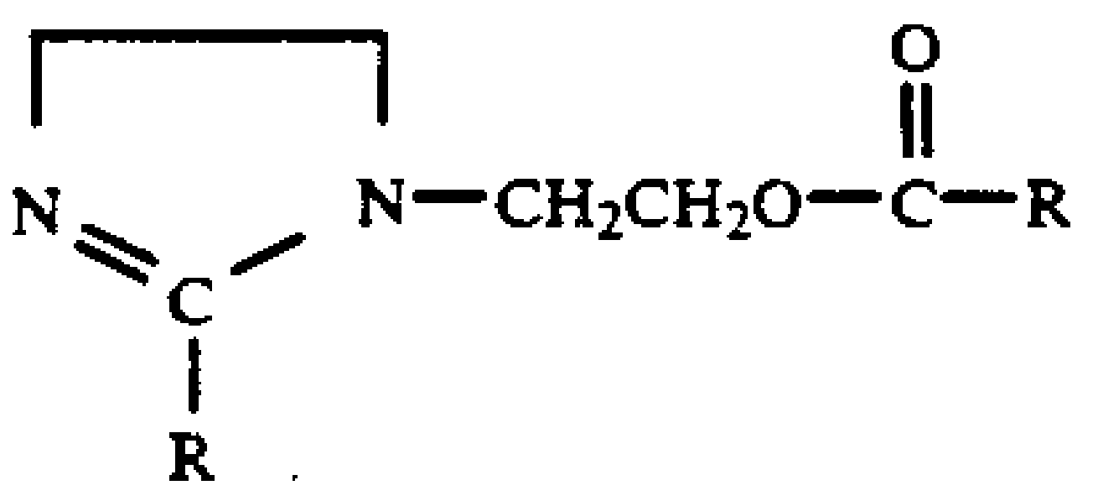
*Softener A is



$$R\overset{O}{\overset{\|}{C}}OCH_2CH_2N^+R(CH_3)_2,\ Cl^-$$

wherein each R group is in the C_{15}-C_{18} alkyl range.

**Softener B is



wherein each R group is in the C_{15}-C_{18} alkyl range.

***Particles prepared according to Example I. 80-100 micron size range; 20% coating weight.

When used in the rinse bath of an automatic washing machine, the coating on perfumed particles of Example III is ruptured and the particles provide a fragrance to the fabrics being treated.

EXAMPLE IV

A liquid laundry detergent composition is as follows:

Component	Weight %
C_{13} linear alkylbenzene sulfonic acid	7.2
C_{14-15} alkyl polyethoxylate (2.25) sulfuric acid	10.8
C_{12-13} alcohol polyethoxylate (6.5)*	6.5
C_{12} alkyl trimethylammonium chloride	1.2
C_{12-14} fatty acid	13.0
Oleic acid	2.0
Citric acid (anhydrous)	4.0
Diethylenetriamine pentaacetic acid	0.23
Protease enzyme (2.0 AU/g)	0.75
Amylase enzyme (375 Am. U/g)	0.16
TEPA-E_{15-18}**	1.5
Monoethanolamine	2.0
(moles of alkanolamine)	(0.033)
Sodium ion	1.66
Potassium ion	2.65
(molar K+:Na+)	(0.94)
Propylene glycol	6.8
Ethanol	7.8
Formic acid	0.66
Calcium ion	0.03

-continued

Component	Weight %
Minors and water	Balance to 100
pH at concentration of 10% in water at 68° F.(20° C.)	8.65

*Alcohol and monoethoxylated alcohol removed.

**Tetraethylene pentaimine ethoxylated with 15–18 moles (avg.) of ethylene oxide at each hydrogen site.

The detergent is prepared by adding the components, with continuous mixing, in the following order: paste premix of alkylbenzene sulfonic acid, sodium hydroxide, propylene glycol and ethanol; paste premix of alkyl polyethoxylate sulfuric acid, sodium hydroxide and ethanol; pentaacetic acid; alcohol polyethoxylate; premix of water, brighteners, alkanolamine and alcohol polyethoxylate; ethanol; sodium and potassium hydroxide; fatty acid; citric acid; formic acid and calcium; alkyl trimethylammonium chloride; TEPA-$E_{15\text{-}18}$; adjust pH to about 8.1; and balance of components.

The above composition is combined with the perfume-containing particles prepared according to Example I as follows. An amount of the perfume particles of Example I (avg. size range 40-150 microns; 5% coating) is thoroughly mixed into the liquid detergent composition so that the detergent composition comprises about 0.3% perfume (about 1% of the detergent composition will comprise the perfume particles).

EXAMPLE V

A fiber- and fabric-softener composition is as follows.

Component	Weight %
Softener C*	3.7
TAMET**	0.3
GMS***	1.20
Phosphoric Acid	0.023
Polydimethylsiloxane (350)	0.10
Glutaraldehyde	550 ppm
Blue Dye	10 ppm
Coated Perfume Particles****	3.0

*$(R^1)_2(CH_3)_2N^-$, Br^-, wherein R^1 is mixed C_{12}–C_{18} alkyl (i.e., "tallowalkyl").

**TAMET is tallowalkyl $N(CH_2CH_2OH)_2$.

***GMS is glyceryl monostearate.

****Coated perfume particles per Example I, sieved to average size less than 100 microns. Coating weight 20%.

It will be appreciated by those skilled in the art that the anions, X, used with any of the cationic fabric softeners herein are a routine matter of choice, and that X can be, for example, chloride, bromide, methylsulfate, and the like. Mixtures of fabric softeners can be used, as can mixtures of anions.

EXAMPLE VI

The fabric softener composition of Example III is modified by using perfumed particles with friable coatings (melamine/urea/formaldehyde; 0.1/1/1.1 mole ratio; 80 micron size) with coating weights of about 20%, respectively. It is to be noted that melamine substitution for about 15% of the urea in the aminoplast coatings is preferred for use in fabric softeners. It is also to be noted that particles above about 80 microns are visible in softener products.

EXAMPLE VII

A detersive bar composition is prepared by gently (so as not to fracture the coating) admixing 2% by weight of the coated perfumed particles of Example I (7% coating; all particles through 150 micron sieve) into a 99.44% tallow soap mixture (Na salt) and formed into a bar in a pin die.

The compositions herein can also be used in combination with abrasives. As is well-known, abrasive cleaners typically comprise 10% to 90+% abrasive such as pumice, silica, calcium carbonate, and the like. Coated perfume particles used in such cleaners are ruptured, in-use, to release their perfume.

EXAMPLE VIII

An abrasive cleanser is as follows.

Component	Weight %
Sodium tallow sulfate	1.0
Calcium carbonate	40.0
Pumice (through 60 micron sieve)	45.0
Sodium sulfate	10.0
Coated perfume particles*	3.0
Chlorinated trisodium phosphate	1.0

*Per Example I; 10% coating; particles through 100 micron sieve.

The composition of Example VIII is prepared by gently dry-blending the ingredients.

It will be appreciated by the formulator that the weight (or thickness) of operable friable coatings can be adjusted according to the usage envisioned. For example, even relatively thick coatings will rupture and release their perfume particles under European machine washing conditions, which can involve wash times of many minutes, at high temperature and considerable agitation. By contrast, USA machine washing conditions are much shorter, and milder, so less coating material should be used. For fabric softeners, agitation and agitation times are usually less than for washing.

EXAMPLE IX

A bleach composition comprises ca. 6% aqueous hypochlorite/ H_2O containing 10% (wt.) of the particles of Example I. The product is shaken prior to use as a clothes bleach or toilet bowl disinfectant to suspend the particles.

EXAMPLE X

A granular laundry detergent is as follows.

Component	Weight %
C_{12} alkylbenzene sulfonate	5.64
Tallow alcohol sulfate	2.42
Sodium sulfate	22.00
Sodium silicate	8.00
Magnesium sulfate	0.40
Carboxymethyl cellulose	0.29
EDTA	0.29
Brightener 47	0.15
Sodium tripolyphosphate	21.34
C_{14-15} EO7 surfactant*	5.00
Sodium perborate $4H_2O$	13.23
Sodium perborate $1H_2$	1.96
Sodium carbonate	7.00
Proteolytic enzyme	0.79
TAED**	3.03
Perfume particles***	1.00
Water/minors	Balance

*As Dobanol 45-7

**Tetraacetylethylenediamine

***Prepared per Example 1; 100–150 micron size; 20% coating

EXAMPLE XI

A concentrated detergent granule is as follows.

Component	Weight %
Sodium linear alkyl benzene sulfonate with an average chain length of 12.4	13.9
Sodium alkylsulfate with an average chain length of 14.5	5.9
Aluminosilicate (Zeolite A; 1-10 micron)	25.36
Polyacrylate 4500	4.47
Polyethylene glycol 8000	1.46
Sodium carbonate	17.82
Sodium sulfate	11.06
Silicate solids	2.05
Brightener 15	0.29
Moisture	7.70
Miscellaneous	0.57
Enzyme	0.78
Nonionic - $C_{12-13}EO_{6.5}$	1.07
Citric acid	6.57
Perfume particles*	1.00

*Per Example I; 100–150 micron size

What is claimed is:

1. A detergent composition, comprising one or more detersive surfactants, optionally, one or more builders, and perfume particles which comprise from about 5% to about 50% by weight of a perfume dispersed in from about 50% to about 95% by weight of a nonpolymeric solid fatty alcohol or fatty ester carrier material, or mixtures thereof, said alcohols or esters having a molecular weight of from about 100 to about 500 and a melting point of from about 37° C. to about 80° C., said alcohols or esters being substantially water-insoluble, said particles having a substantially water-insoluble friable coating on their outer surfaces, said coated particles having an average size less than about 350 microns.

2. A composition according to claim 1 wherein the average size of the coated particles is not greater than 150 microns.

3. A composition according to claim 2 wherein the friable coating is an aminoplast polymer.

4. A composition according to claim 3 wherein the coating is the reaction product of an amine selected from urea and melamine, or mixtures thereof, and the aldehyde is selected from formaldehyde, acetaldehyde, glutaraldehyde, or mixtures thereof.

5. A composition according to claim 4 wherein the coating comprises 1% to 30% by weight of the particles.

6. A composition according to claim 5 wherein the carrier material comprises an alcohol selected from the C_{14}–C_{18} alcohols.

7. A composition according to claim 5 wherein the carrier material is an ester comprising at least 18 carbon atoms.

8. A composition according to claim 1 in bar form.

9. A composition according to claim 1 which additionally comprises an abrasive.

* * * * *